Altering the Structural Properties of $A_2B_{12}H_{12}$ Compounds via Cation and Anion Modifications

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Abstract

The recent discovery of unusually high cationic conductivity in $Na_2B_{12}H_{12}$ above its entropy-driven, order-disorder phase transition near 529 K and the expected similar conductivity behavior in $Li_2B_{12}H_{12}$ above its transition near 615 K have led us to investigate modifications of these two materials in an effort to reduce their transition temperatures and thus extend their high conductivities to more technologically favorable values. Differential scanning calorimetry measurements of perhalogenated $Na_2B_{12}X_{12}$ ($X=Cl$ and I), which are larger anion relatives of $Na_2B_{12}H_{12}$, suggest unfavorably higher transition temperatures near 730 K and 816 K, respectively. New mixed-cation $Li_yNa_{2-y}B_{12}H_{12}$ phases show intermediate transition temperatures between those of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$. X-ray diffraction measurements and neutron vibrational spectra corroborate low-temperature ordered structures (for $y=0.67$, 1, and 1.33) similar to $Li_2B_{12}H_{12}$, with Li^+ and Na^+ disordered among the near-trigonal cation sites.

Keywords

Borohydrides; order-disorder phase transition; superionic conductivity; ionic modification; perhalogenated dodecaborate; dodecahydro-*closo*-dodecaborate

1. Introduction

The continuous search for stable solid-state electrolytes applicable towards Li-ion and Na-ion batteries has fueled research on desirable new fast-ion conductors based on complex hydrides [1 – 3]. For example, earlier electrical conductivity studies of $LiBH_4$ performed by Matsuo *et al.* showed a three-fold increase in Li^+ conductivity to values exceeding $10^{-3} \text{ S cm}^{-1}$ following the orthorhombic ($Pnma$) to hexagonal ($P6_3mc$) phase transition near 390 K [4, 5]. More recently, Udovic *et al.* investigated the structural and conductive properties of sodium dodecahydro-*closo*-dodecaborate ($Na_2B_{12}H_{12}$) [6]. This compound displayed superionic conductivity of more than 0.1 S cm^{-1} above 540 K, upon transforming from the room-temperature ordered monoclinic ($P2_1/n$) to the high-temperature disordered cubic phases ($Pm\bar{3}n$ and $Im\bar{3}m$) near 529 K [6 – 10]. The sudden enhancement in ionic

conductivity within this borohydride material coincides with the appearance of a cation-vacancy-rich sublattice within spacious interstitial corridors formed by the unusually large and orientationally mobile icosahedral $B_{12}H_{12}^{2-}$ anions [7, 8]. Such less restrictive pathways enable more facile cation diffusional jumps [9, 10]. $Li_2B_{12}H_{12}$ was also observed to undergo an order-disorder phase transition near 615 K from a pseudo-fcc ($Pa\bar{3}$) lattice to an expanded fcc lattice with extensive cation and anion disorder [8, 11, 12], but slow compound degradation once in the disordered phase hindered the measurement of probable superionic behavior.

Since there is a correlation between the solid-state phase transition temperature and conductivity in these systems, the onset of superionicity can be potentially lowered by minor alterations in the cations and anions. From a practical viewpoint, it is desirable that potential solid electrolytes incorporated into future battery technologies should possess fast-ion conductive behavior at or below room temperature. Herein we explore the effect of anionic or cationic modifications of $Na_2B_{12}H_{12}$ on its phase behavior. The $B_{12}H_{12}^{2-}$ anion was first modified by substitution of hydrogen with a halogen to form perhalogenated dodecaborate compounds, $Na_2B_{12}X_{12}$, where $X=Cl$ and I . Alternatively, partial substitution of the Na^+ by Li^+ cations was performed to produce mixed solid-solution $Li_yNa_{2-y}B_{12}H_{12}$ phases.

2. Materials and Methods

$Na_2B_{12}H_{12}$, $Na_2B_{12}Cl_{12}$, $Na_2B_{12}I_{12}$ and $Li_2B_{12}H_{12}$ are commercial products obtained from Katchem [13]. $Na_2B_{12}X_{12}$ ($X=Cl$ and I) samples were used without further purification. $Li_yNa_{2-y}B_{12}H_{12}$ ($y=0.67, 1$, and 1.33) samples were synthesized by dissolving stoichiometric amounts of anhydrous $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ in 10 ml of deionized water. A two-step drying process was then performed: 1) the excess water was removed by pumping the mixture under dynamic vacuum (*ca.* 10^{-2} Pa) at room temperature for two days; 2) the wet paste was heated at 473 K under dynamic vacuum (*ca.* 10^{-4} Pa) overnight to remove any traces of water, and dry white powders were obtained. Subsequent dry-sample manipulations were performed in a He-filled glovebox.

DSC measurements with simultaneous thermogravimetric analysis (TGA) were performed on all samples using a Netzsch (STA449 F1 Jupiter) TGA-DSC under He flow with Al or Al_2O_3 sample pans and temperature ramp rates between ± 10 to 20 K/min. X-ray powder diffraction (XRPD) data were collected on a Rigaku Ultima III X-ray diffractometer coupled with a Cu-K α source on the dry $Li_yNa_{2-y}B_{12}H_{12}$ samples sealed in 0.7 mm glass capillaries over 24 h at room temperature in the 2θ range of 10 - 60° with a step size of 0.02° . All structural Rietveld refinement analyses were performed using the Fullprof Suite software package [14, 15]. The structures were visualized using the VESTA (Visualization for Electronic and Structural Analysis) software [16]. A neutron vibrational spectrum of $LiNaB_{12}H_{12}$ was measured at 4 K using the BT-4 Filter-Analyzer Neutron Spectrometer [17] at the NIST Center for Neutron Research with the Cu(220) monochromator and both pre- and post-monochromator horizontal collimations of $20'$ of arc. All error bars in the figures represent $\pm 1 \sigma$. Where no error bars are shown, the standard uncertainties are commensurate with the observed scatter in the data.

3. Results and Discussions

3.1 Anionic Modifications

The DSC scans of the $\text{Na}_2\text{B}_{12}\text{X}_{12}$ ($\text{X} = \text{Cl}$ and I) samples are compared with that for $\text{Na}_2\text{B}_{12}\text{H}_{12}$ in Fig. 1. A reversible phase transition is observed for both compounds, with endothermic peaks on heating and exothermic peaks on cooling. However, the changes in both compounds occur at higher temperatures as compared to $\text{Na}_2\text{B}_{12}\text{H}_{12}$ [8]. There appears to be a correlation between the anion radius and the transition temperatures on both heating and cooling, with the larger anions resulting in higher transition temperatures. This suggests that the transition temperature may increase with decreasing cation/anion size ratio. This was seen to be the case for the heavier isotypical $\text{A}_2\text{B}_{12}\text{H}_{12}$ ($\text{A} = \text{K}$, Rb , and Cs) compounds where the order-disorder transition temperature was found to decrease with increasing cation radius (*i.e.* increasing cation/anion size ratio) [19]. Likewise, it was observed for the series of alkali-metal tetrahydroborates ABH_4 ($\text{A} = \text{Li}$, Na , K , Rb , and Cs), where again the increase in cation radius was found to lower the order-disorder phase transition temperature [20]. This is somewhat at odds, however, with the scattered order-disorder transition temperatures observed for the $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ [21] and $\text{Cs}_2\text{B}_{12}\text{X}_{12}$ ($\text{X} = \text{Cl}$, Br , and I) [22] compounds through DTA/TG and DSC analysis by Tiritiris *et al.*, where there is no clear indication of how anionic size variations affect the transition temperatures. All order-disorder transition temperatures are summarized in Table 1. It would be interesting to further extend these comparisons to include perhalogenated dodecaborates containing fluorinated $\text{B}_{12}\text{F}_{12}^{2-}$ anions, which have also been successfully synthesized and found to be thermally stable. [23]

3.2 Cationic Modifications

The PXRD refinement results for the dry $\text{Li}_y\text{Na}_{2-y}\text{B}_{12}\text{H}_{12}$ ($y = 0.67$, 1 , and 1.33) samples are shown in Fig. 2. All three compounds crystallize in the same $P\bar{a}3$ cubic space group, as found for $\text{Li}_2\text{B}_{12}\text{H}_{12}$. [11] The PXRD patterns look very similar to each other, with just minor shifts in 2θ angles and intensities of certain peaks. The diagram insets in Fig. 2 for each phase show a zoom ($14.5 - 16.5^\circ$) of the main peak corresponding to the (111) reflection. Compared to $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (black dotted line), this peak is clearly shifted towards lower 2θ angles with increasing Na substitution. Hence, without much surprise, the unit cell parameter a increases accordingly: $9.5771(2)$ for $\text{Li}_2\text{B}_{12}\text{H}_{12}$ [11], $9.725(2)$ for $\text{Li}_{1.33}\text{Na}_{0.67}\text{B}_{12}\text{H}_{12}$, $9.820(3)$ for $\text{LiNaB}_{12}\text{H}_{12}$, and $9.9274(18)$ for $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$. The structural refinement data for these phases are summarized in Table 2. During the Rietveld refinement for all three compounds, the Li and Na occupations on the $8c$ Wyckoff site were allowed to vary, and the results are close to that of the starting synthesis stoichiometry of Li and Na (*cf.* Table 2). As a visual example, the structural projection of the cubic ($P\bar{a}3$) $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$ unit cell along the $[100]$ direction is shown in Fig. 3, with an approximate Li (cyan) to Na (yellow) ratio of 1:2.

The 4 K neutron vibrational spectrum for $\text{LiNaB}_{12}\text{H}_{12}$ is compared with those for $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ in Fig. 4. Previous first-principles phonon calculations of the alkali and alkaline-earth dodecahydro-*clos*-

dodecaborate compounds confirm that the vibrational spectrum is noticeably sensitive to the cation and anion structural arrangements [24]. Aside from minor differences, the $\text{LiNaB}_{12}\text{H}_{12}$ spectrum is rather similar to that for $\text{Li}_2\text{B}_{12}\text{H}_{12}$, which is consistent with the $Pa\bar{3}$ structural symmetry determined by diffraction.

The DSC characterization results for the dry $\text{Li}_y\text{Na}_{2-y}\text{B}_{12}\text{H}_{12}$ samples are shown in Fig. 5. Similar to the starting individual pure phases of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ [8], a reversible phase transition is observed for all three compounds, with endothermic peaks on heating and exothermic peaks on cooling. The phase transition temperatures occur between the pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ values. There is a trend of lower transition temperatures with increasing Na substitution, with a very rapid drop by replacing 1/3 of the Li with Na, *i.e.*, $\text{Li}_{1.33}\text{Na}_{0.67}\text{B}_{12}\text{H}_{12}$. Also, the phase transition peaks become broader with increasing Na substitution.

4. Conclusion

$\text{Na}_2\text{B}_{12}\text{X}_{12}$ ($\text{X} = \text{Cl}$ and I) perhalogenated *closo*-dodecaborate phases were characterized by DSC, showing reversible solid-state phase transitions, with temperatures shifted to higher values for larger anions. From these results, we conclude that any modifications involving larger anion substitutions push the transition temperature in an undesirable direction, and future efforts will focus on substituting smaller anions into the structure. Structural characterizations are currently underway to understand the low-temperature and high-temperature phases for both halogenated compounds, and prospective electrochemical studies are also planned.

Cationic substitution via the mixing of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ salts in different ratios yielded mixed-alkali solid solutions. From Rietveld model refinements of the PXRD data, the dodecahydro-*closo*-dodecaborate phases crystallized in the same $Pa\bar{3}$ cubic space group (as $\text{Li}_2\text{B}_{12}\text{H}_{12}$), with larger unit cell parameters for larger Na/Li ratios. Qualitative analysis of the neutron vibrational spectra shows similarities between the $\text{LiNaB}_{12}\text{H}_{12}$ and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ phases. DSC showed the phase transition temperatures to be within the range set by the two starting pure phases, $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$. This is consistent with the observed correlations to date between order-disorder phase transition temperature and cation/anion size ratio. Although these modifications result in higher transition temperatures than for pure $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and are not favorable with respect to the Na^+ cations, they are positive modifications with respect to the Li^+ cations since they result in lower transition temperatures than for pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$. Future efforts will focus on increasing the cation/anion size ratio further by substituting other larger cations into both $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ structures in an attempt to attain ever lower order-disorder transition temperatures.

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Figure Captions:

Figure 1: The DSC results for a) $\text{Na}_2\text{B}_{12}\text{Cl}_{12}$ (blue) and b) $\text{Na}_2\text{B}_{12}\text{I}_{12}$ (grey) with a ramping rate of 20 K min^{-1} for both heating and cooling, under He gas flow. The brown dotted line shows the position of the peak transition temperature of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ on heating [8].

Figure 2: The Rietveld analysis of the PXRD (Cu-K_α source) data performed on the mixed alkali dodecahydro-*closo*-dodecaborate phases at room temperature: a) $\text{Li}_{1.33}\text{Na}_{0.67}\text{B}_{12}\text{H}_{12}$, b) $\text{LiNaB}_{12}\text{H}_{12}$, and c) $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$, cf. Table 2. Diagram insets: A zoom on the $P\bar{a}3$ (111) 2θ peak for the respective phases, with comparison to the corresponding peak of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (black dotted line) [11].

Figure 3: Structural projection of the cubic ($P\bar{a}3$) $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$ unit cell along the [100] direction. Spheres key: Li (cyan), Na (yellow), B (green) and H (pink). The $8c$ Wyckoff site is occupied as per the stoichiometry of Li and Na, cf. Table 2c.

Figure 4: The neutron vibrational spectra at 4 K of a) $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (black), b) $\text{LiNaB}_{12}\text{H}_{12}$ (purple), and c) $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (brown). The spectra of the pure phases are obtained from ref 24, shown here for comparison.

Figure 5: The DSC results for a) $\text{Li}_{1.33}\text{Na}_{0.67}\text{B}_{12}\text{H}_{12}$ (red), b) $\text{LiNaB}_{12}\text{H}_{12}$ (purple), and c) $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$ (green) with a ramping rate of 10 Kmin^{-1} for both heating and cooling, under He gas flow. The black and brown dotted lines show the positions of the peak transition temperatures of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$, respectively, on heating [8].

Table 1: The cation and anion radii (r_c and r_a), calculated r_c/r_a ratio, coordination number and order-disorder phase transition temperatures (T_{trans}) for a) $\text{Na}_2\text{B}_{12}\text{X}_{12}$, X = H, Cl and I; and b) $\text{A}_2\text{B}_{12}\text{H}_{12}$, A = Li, Na, K, Rb and Cs.

Table 2: Structural refinement data for the cubic ($P\bar{a}3$) mixed-alkali dodecahydro-*closo*-dodecaborate phases with a) $\text{Li}_{1.33}\text{Na}_{0.67}\text{B}_{12}\text{H}_{12}$, b) $\text{LiNaB}_{12}\text{H}_{12}$, and c) $\text{Li}_{0.67}\text{Na}_{1.33}\text{B}_{12}\text{H}_{12}$.

Figure 1

Figure 2

Figure 3

4 K

Figure 4

Figure 5

Tables

a) Na ₂ B ₁₂ X ₁₂						
X	<i>r_c</i> (Å) [18]	<i>r_a</i> (Å) [8]	<i>r_c/r_a</i>	Coordination	<i>T</i> _{trans-heating} (K)	<i>T</i> _{trans-cooling} (K)
H	0.99*	3.28	0.30	4	529 [8]	477 [8]
Cl	0.99*	4.19	0.24	-	730	696
I	0.99*	4.74	0.21	-	816	772

b) A ₂ B ₁₂ H ₁₂					
A	<i>r_c</i> (Å) [18]	<i>r_a</i> (Å) [8]	<i>r_c/r_a</i>	Coordination	<i>T</i> _{transition} (K)
Li	0.59*	3.28	0.18	4	615 [8]
Na	0.99*	3.28	0.30	4	529 [8]
K	1.38^	3.28	0.42	6	811 [19]
Rb	1.52^	3.28	0.46	6	742 [19]
Cs	1.67^	3.28	0.51	6	529 [19]

c) Cs ₂ B ₁₂ X ₁₂					
X	<i>r_c</i> (Å)	<i>r_a</i> (Å) [8]	<i>r_c/r_a</i>	Coordination	<i>T</i> _{transition} (K)
H	1.67^ [18]	3.28	0.51	6	529 [19]
Cl	1.60* [8]	4.19	0.38	4	453 [22]
Br	1.60* [8]	4.43	0.36	4	585 [22]
I	1.60* [8]	4.74	0.34	4	531 [22]

* IV coordination, ^ VI coordination

Table 1

a) For y = 1.33, Li _{1.33} Na _{0.67} B ₁₂ H ₁₂ : Cubic $P\bar{a}3$ (No. 205) , <i>i.e.</i> Li-rich phase						
a = b = c = 9.7248(7) Å		V = 919.70(12) Å ³		$\chi^2 = 1.80$	R _{wp} = 16.2	Li _{1.33} Na _{0.67} B ₁₂ H ₁₂ = 97(2)
$\alpha = \beta = \gamma = 90^\circ$		Z = 4		R _p = 19.8	R _{Bragg} = 2.44	Na ₂ B ₁₂ H ₁₂ = 3.3(2)
Atom	x	y	z	B _{iso}	Occ.	Site
Li1	0.3668(8)	0.3668(8)	0.3668(8)	5.9(7)	0.66(2)	8c
Na1	0.3668(8)	0.3668(8)	0.3668(8)	5.9(7)	0.34(2)	8c
B1	0.0901(10)	0.4120(12)	0.3784(10)	0.8(4)	1 (-)	24d
B2	0.0360(9)	0.0383(10)	0.1670(8)	0.8(4)	1 (-)	24d
H1	0.155(2)	0.349(2)	0.2913(19)	0.8(4)	1 (-)	24d
H2	0.061(2)	0.068(3)	0.2857(15)	0.8(4)	1 (-)	24d

b) For y = 1, LiNaB ₁₂ H ₁₂ : Cubic $P\bar{a}3$ (No. 205)						
a = b = c = 9.8200(12) Å		V = 947.0(2) Å ³		$\chi^2 = 1.22$	R _{wp} = 18.7	LiNaB ₁₂ H ₁₂ = 93(3)
$\alpha = \beta = \gamma = 90^\circ$		Z = 4		R _p = 23.3	R _{Bragg} = 2.77	Na ₂ B ₁₂ H ₁₂ = 7.3(5)
Atom	x	y	z	B _{iso}	Occ.	Site
Li1	0.3649(7)	0.3649(7)	0.3649(7)	5.6(7)	0.47(4)	8c
Na1	0.3649(7)	0.3649(7)	0.3649(7)	5.6(7)	0.53(4)	8c
B1	0.0875(13)	0.4106(14)	0.3800(12)	2.2(8)	1 (-)	24d
B2	0.0376(12)	0.0361(12)	0.1663(10)	2.2(8)	1 (-)	24d
H1	0.148(2)	0.344(2)	0.295(2)	2.2(8)	1 (-)	24d
H2	0.063(2)	0.065(3)	0.2825(15)	2.2(8)	1 (-)	24d

c) For y = 0.67, Li _{0.67} Na _{1.33} B ₁₂ H ₁₂ : Cubic $P\bar{a}3$ (No. 205), <i>i.e.</i> Na-rich phase						
a = b = c = 9.9274(6) Å		V = 978.37(11) Å ³		$\chi^2 = 1.44$	R _{wp} = 16.3	Li _{0.67} Na _{1.33} B ₁₂ H ₁₂ = 88(2)
$\alpha = \beta = \gamma = 90^\circ$		Z = 4		R _p = 19.2	R _{Bragg} = 2.69	Na ₂ B ₁₂ H ₁₂ = 11.6(3)
Atom	x	y	z	B _{iso}	Occ.	Site
Li1	0.3620(5)	0.3620(5)	0.3620(5)	6.1(5)	0.33(2)	8c
Na1	0.3620(5)	0.3620(5)	0.3620(5)	6.1(5)	0.67(2)	8c
B1	0.0833(10)	0.4110(12)	0.3809(9)	2.5(4)	1 (-)	24d
B2	0.0390(9)	0.0353(9)	0.1656(8)	2.5(4)	1 (-)	24d
H1	0.141(2)	0.341(2)	0.2962(18)	2.5(4)	1 (-)	24d
H2	0.063(2)	0.060(3)	0.2793(14)	2.5(4)	1 (-)	24d

Table 2

Graphical abstract